# A simple way to construct the exact optimized effective potential for orbital functionals, including exact exchange

STEPHAN KÜMMEL AND JOHN P. PERDEW
Department of Physics and Quantum Theory Group
Tulane University, New Orleans, Louisiana 70118

The exact exchange energy of density functional theory is a prominent example for an implicit density functional: it depends explicitly on the Kohn-Sham orbitals and thus (only) implicitly on the density. For all functionals that are explicit orbital functionals, the corresponding exchange-correlation potential cannot be calculated directly as the functional derivative of the exchange-correlation energy with respect to the density. Instead, it must be obtained as the solution of the optimized effective potential (OEP) integral equation. This is computationally very demanding and has limited the use of third-generation density functionals which use the exact exchange energy in self-consistent Kohn-Sham calculations.

We demonstrate that the exact OEP can be constructed without explicitly solving the OEP integral equation. Instead, for each occupied Kohn-Sham orbital we calculate a corresponding "orbital shift". The exact OEP can then be obtained iteratively by solving a system of partial differential equations instead of an integral equation. No unoccupied orbitals need to be calculated explicitly, and the iteration converges very quickly within a few steps. Solving the orbital shift equations is computationally roughly as cheap as calculating the Hartree potential.

We tested the accuracy of this new method by calculating total energies and Kohn-Sham eigenvalues of atoms using the exact exchange energy. Our results agree with the results obtained by direct solution of the integral equation. We investigated the influence of the exact exchange energy on more complex systems by calculating total energies, Kohn-Sham eigenvalues and static electric polarizabilities of three-dimensional sodium clusters. Our calculations show that, contrary to common believe, the exact exchange potential does not approach $-1/r$ everywhere in the asymptotic region of finite systems, confirming recent findings in the context of the localized Hartree-Fock method by Della Sala and Görling [J. Chem. Phys. **116**, 5374 (2002)]. We will also try to answer the long-standing question whether the wrong asymptotic fall-off of the LDA potential influences the static electric polarizability.